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**CRYSTAL STRUCTURE OF TETRA-AMMONIUM ADAMANTYL  
TETRA-NITRATE (TAATN): HIGH ENERGY/DENSITY FUEL  
CANDIDATE FOR LIQUID PROPELLANT**

A. J. Bracuti

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## ERRATA

TECHNICAL REPORT ARAED-TR-89025

CRYSTAL STRUCTURE OF TETRA-AMMONIUM ADAMANTYL  
TETRA-NITRATE (TAATN): HIGH ENERGY/DENSITY FUEL  
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A. J. Bracuti

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Change text of report as follows:

Replace paragraph 6 on page 1 with the following:

Despite the successful utility of LP1845 and LP1846 in various test fixtures, these propellants may not, in fact, have universal applicability or meet the requirements for future RLPG modifications. Some LP properties to consider with respect to future RLPG requirements are impetus, density, and chemical compatibility.

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## CONTENTS

	Page
Introduction	1
Experimental	3
X-Ray Diffraction Data Collection	3
Data Reduction	3
Structure Determination	4
Results and Discussion	5
Description of the Nitrate Anion	5
Description of the TAA Cation	5
Conclusions	7
Recommendations	8
References	15
Distribution List	17

## TABLES

1	Selected properties of LP1846	9
2	Atomic structures and Beq for TAATN and their esd's	9
3	Thermal parameters for TAATN and their esd's	10
4	Details of hydrogen bonding with distance in angstroms (A) angles in degrees	10
5	Close heavy atom non-hydrogen bonded interionic distances and their esd's	10
6	Bond lengths and bond angles and their esd's in parentheses	11
7	Torsion angles and their esd's for TAA cation	12
8	Nitrate ion best least-squares-plane data and their esd's	12

## INTRODUCTION

Currently, a new large caliber liquid propellant weapon system is under development by the Army which uses spray injection to control propellant burning and resultant ballistic performance. This system known as the regenerative liquid propellant gun (RLPG) presently uses either of two water-based liquid propellants (LP) which were formulated and developed at the BRL and designated as LP1845 and LP1846 (ref 1).

Both liquid propellants contain the same ratio of dissolved oxidizer to fuel salts but differ only in their concentration of water. The oxidizer in both cases is hydroxyl ammonium nitrate (HAN) whose molecular formula is  $\text{HONH}_3\text{NO}_3$  while the fuel is triethanol ammonium nitrate (TEAN) whose molecular formula is  $(\text{C}_2\text{H}_4\text{OH})_3\text{HN NO}_3$ .

The oxidizer to fuel ratio (7:1) for these HAN-based liquid propellants was fixed at the theoretical stoichiometry required for complete oxidation of the LP during combustion. In this way, only  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{H}_2\text{O}$  should theoretically be the final combustion products if equilibrium is attained in the combustion chamber.

Specifically, LP1845 contains 63.23% HAN, 19.96% TEAN, and 16.83% water while LP1846 contains 60.79% HAN, 19.19% TEAN, and 20.02% water (all weight percentages). It was assumed that adjusting the water concentration would affect propellant sensitivity, flame temperature, and impetus without affecting propellant combustion chemistry. This would then provide a relatively simple means to tailor this HAN-based liquid propellant for different specific purposes.

Since both of these propellants have been used successfully in a variety of test fixtures, it has been decided by the Army that one of them will be the candidate for use in RLPG artillery systems. In fact, a demonstration of a 155-mm RLPG using LP1846 has been scheduled for the second half of FY91.

Despite the successful utility of LP1845 and LP1846 in various test fixtures, these propellants may not, in fact, have universal applicability or meet the requirements for future RLPG requirements are impetus, density, and chemical compatibility.

The data in table 1 reveal that LP1845 and LP1846 have impetus values of 934 and 892 J/g (MCVEC equilibrium code, ref 2) and density values of 1.44 and 1.40  $\text{g/cm}^3$ , respectively. These values are satisfactory for present artillery systems, but may be inadequate for use in direct fire application and for future high energy systems. Chemical compatibility is presently being addressed in the ARDEC 6.3a LP program, and although no conclusive data are presently available, selected transition metals appear to be incompatible with the LP above specific concentration limits.

How then can the present liquid propellants be improved? One obvious answer is to increase the energy density of the propellant. This can be accomplished by increasing the impetus or density by changing either the oxidizer or fuel. In seeking a new oxidizer or fuel for this system, however, one is constrained to use ingredients which improve performance without altering those HAN-like properties required by the RLPG. Some of these necessary properties are water miscibility, low sensitivity, efficient pumpability, and wide-range chemical compatibility.

Use of an alternate oxidizer could eliminate the transition metal compatibility problem and perhaps increase the energy density, but finding one, however, that is both water miscible and as efficient an oxidizer as HAN would be extremely difficult. Therefore, a more viable approach would be the use of an alternate fuel.

Guided by these objectives and constraints, a program was initiated at ARDEC to synthesize high density/high impetus compounds for use as potential LP fuel candidates. Caged molecules were selected because they could provide both higher energies and densities and because ARDEC concurrently has an ongoing cage molecule synthesis program. At the outset, however, the relatively strainless adamantane (based on molecular modeling) was chosen as the precursor caged molecule rather than the highly strained but more energetic cubane. The rationale for this was that highly strained molecules probably have greater propensities for detonation which may be desirable for explosive but not for propellants.

The initial candidate fuels selected were tetra-ammonium adamantyl tetra-nitrate ( $C_{10}H_{24}N_8O_{12}$ , TAATN) and tetra-ammonium tetra-nitro adamantyl tetra-nitrate ( $C_{10}H_{20}N_{12}O_{20}$ , TATHATN). These candidates were to be synthesized from adamantane ( $C_{10}H_{16}$ ) in a step-wise synthesis scheme in which TAATN was the target intermediate and TATNATN was the target final product. The strategy used here was to first produce a water soluble adamantane salt which could serve both as a possible fuel candidate and as a precursor for synthesis of even higher energy fuel candidates.

An intermediate compound, presumed to be TAATN, was synthesized from adamantane. There is always some question if the cage molecule remains intact throughout a series of reactions in any given synthetic scheme. In order to determine unequivocally that this compound was, indeed, the target TAATN, a single-crystal x-ray diffraction investigation was initiated to determine its molecular structure.

## EXPERIMENTAL

### X-Ray Diffraction Data Collection

An opaque white crystal of TAATN synthesized at ARDEC having approximate dimensions of 0.200 x 0.209 x 0.200 mm was mounted on a glass fiber. The preliminary examination and data collection were performed with Cu K $\alpha$  x-radiation ( $\lambda = 1.54178$  Å) on a Rigaku ASC5r computer controlled diffractometer equipped with a graphite crystal incident-beam monochromator and a 12 kw rotating anode generator. The data was collected at -115°C rather than at room temperature in order to optimize the intensity data measurements.

Cell constants and orientation matrix for data collection were obtained from least-squares refinement using the setting angles of 25 reflections in the angular range of  $40.07 < 2\theta < 58.06$ . As a check on crystal quality, omega scans of several intense reflections were measured. The width at reflection intensity half-height of each reflection was 0.32 with a take-off angle 6.0 which indicates good crystal quality.

The intensity data were collected at a temperature of  $-115 \pm 1^\circ\text{C}$  using the  $\omega - 2\theta$  technique with a scan rate of 32/min (in omega). To assure good counting statistics, the intensities of weak reflections [ $I < 10 \sigma(I)$ ] were measured by accumulating the counts from two successive rescans. Intensity data for 447 reflections with  $h = 0$  to 11, and  $k = 0$  to 10 were collected to a maximum  $2\theta$  value of 120.0. The scan range (in degrees) was determined as a function of  $\theta$  to correct for the separation of the K $\alpha$  doublet. The scan width was calculated with the equation.

$$\theta \text{ scan width} = 1.3 + 0.300 \tan \theta$$

The background level was determined by recording the counts at a fixed position on each side of the reflection. The ratio of peak counting-time to background counting-time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 40 cm.

### Data Reduction

Lorentz - polarization and absorption corrections but no secondary extinction corrections were applied to the intensity data. The empirical absorption corrections based on the linear absorption coefficient for Cu K $\alpha$  transmission factors ranging from 0.93 to 1.00.



As a check on crystal and electronic stability, three representative reflections were measured after every 150 reflections. No decay correction was applied to the reflection data-set because the intensities of these monitored reflections remained constant within experimental error throughout data collection.

The crystal data are

Tetragonal, space group  $P\bar{4}2_1c$  (#114),  $a = 10.046(1)$ ,  $c = 8.980(2)$  Å

$V = 906.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.643$  g/cm<sup>3</sup>,  $U = 12.59$  cm<sup>3</sup>,  $F(000) = 472$

$F_w = 448.35$ ,  $T = 158$  K (-115°C), systematic absences:  $h00$ ,  $h = 2n + 1$ ;  
 $hh\ell$ ,  $\ell = 2n + 1$ .

On the basis of the systematic absences

$$h00 \quad h = 2n + 1$$

$$hh\ell \quad \ell = 2n + 1$$

and later confirmed by the successful solution and refinement of the structure the non-centrosymmetric space group is  $P\bar{4}2_1c$  (#114).

## Structure Determination

The positions of the non-hydrogen atoms were found by direct methods (ref 3) and the hydrogen atoms were located by difference Fourier techniques. The hydrogen atoms were refined isotropically while the non-hydrogen atoms were refined anisotropically by full-matrix least-squared in which the function  $w(\sum |F_o| - |F_c|)^2$  was minimized and  $w$  is defined as  $4F_o/(F_o^2)$ .

The standard deviation on intensities,  $(F_o^2)$ , is defined

$$\sigma^2(F_o^2) = [S^2(C + R^2B) + (p F_o^2)] (Lp)^2$$

in which  $S$  is the scan rate,  $C$  is the total integrated peak count,  $B$  is the total background count,  $R$  is the ratio of the scan time to the background count,  $Lp$  is the Lorentz and polarization factor, and the parameter  $p$  is a factor introduced to down-weight the intense reflections. In this case  $p$  was set to 0.050.

The x-ray scattering factors were taken from Cromer and Waber (ref 4). Anomalous dispersion effects were included in the calculation of structure factors (ref 5) and the values of  $f'$  and  $f''$  were those of Cromer (ref 6). Only 401 reflections having intensities greater than 3.0 times their standard deviations were used in the refinement.

of the trial structure. The final cycle of refinement included 91 variables which converged (largest parameter shift was 0.00 times its esd) with an unweighted agreement factor of  $R = 0.038$

$$R = \sum |F_o| - |F_c| / \sum |F_o|$$

and a weighted agreement factor of  $R_w = 0.047$  in which

$$R_w = \text{SQRT} \left[ \left( \sum w (|F_o| - |F_c|)^2 / \sum w F_o^2 \right) \right]$$

The standard deviation of an observation of unit weight was 1.76. The maximum and minimum peaks in the final difference Fourier were 0.19 and -0.36 e/A<sup>3</sup>, respectively.

## RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters of TAATN are presented in table 2 and table 3, respectively. Details of the hydrogen bonding are given in table 4 and close non-hydrogen bonded interionic distances are presented in table 5. The bond lengths and bond angles are listed in table 6 while torsion angles are presented in table 7. The best least-squares-plane data for the nitrate anion are listed in table 8. Both the TAA cation and nitrate anion as well as the atom numbering scheme are depicted in figure 1 and the unit cell of TAATN is presented in figure 2.

The title compound crystallizes in the tetragonal space group  $P\bar{4}2_1c$  with  $a = 10.046(1)$  and  $c = 8.980(2)$  Å. The atomic coordinates for the TAATN asymmetric unit which contains three non-equivalent carbon atoms, one nitrogen atom, six non-equivalent hydrogen atoms and one nitrate anion containing one nitrogen atom and three non-equivalent oxygen atoms, are presented in table 2.

The symmetry elements of this space group operating on the asymmetric group generate all the atoms necessary to form two formula weights, each consisting of one TAA cation and the four nitrate anions. The C(2) atom lies on a special position which generates three additional equivalent carbon atoms while two other non-equivalent hydrogen atoms of the cation also occupy general positions and as a result seven additional nitrogen atoms and 42 hydrogen atoms are generated.

With respect to the nitrate anion, there are one nitrogen and three non-equivalent oxygen atoms occupying eight-fold general positions which generate seven additional nitrogen atoms and 21 oxygen atoms. The space group symmetry operations produce

a unit cell which contains 20 carbon atoms, 40 hydrogen atoms, 16 nitrogen atoms, and 24 oxygen atoms. Since there are two formula weights per unit cell, this results in a compound with a molecular formula of  $C_{10}H_{24}N_4 \cdot (NO_3)_4$  which has a calculated x-ray density of  $1.545 \text{ g/cm}^3$ .

In this compound each cation is surrounded by 12 hydrogen bonded nearest-neighbor anions, while each anion is surrounded by three hydrogen bonded nearest-neighbor cations (fig. 1). The closest non-hydrogen bonded interionic distance between adjacent cations [ $C(1)-C(1)$ , table 5] is  $2.470(5)$  while the closest hydrogen bonded interionic contact between dissimilar ions is  $2.799(4)$  Å [ $N(1)-O(3)$ , table 4] with a hydrogen bond length [ $H(2)-O(3)$ ] of  $1.84(6)$  Å and a bond angle [ $N(1)-H(2)-O(3)$ ] of  $164(4)$  degrees. The remaining two hydrogen-bonded interionic closest-contacts are:  $N(1)-O(2)$  with a distance of  $2.914$  Å, a hydrogen bond length of [ $H(1)-O(2)$ ] of  $2.11(4)$  Å and bond angle [ $N(1)-H(1)-O(2)$ ] of  $160(4)$  degrees; and  $N(1)-O(1)$  with a distance of  $2.920$  Å, a hydrogen bond length of [ $H(3)-O(1)$ ] of  $1.20(6)$  Å and bond angle [ $N(1)-H(3)-O(1)$ ] of  $163(5)$  degrees.

### Description of the Nitrate Anion

The nitrate ion is planar (table 8) and displays  $D_{3h}$  symmetry since the three respective  $N(2)-O(1)$ ,  $N(2)-O(2)$ , and  $N(2)-O(3)$  distances (table 5) of  $1.248(4)$ ,  $1.257(4)$ , and  $1.256(4)$  and their associated angles are equivalent (mean value  $120$  degrees).

### Description of the TAA Cation

Adamantane, itself, is a caged molecule composed of four chair-conformed cyclohexane rings ( $C_6H_{12}$ ) which are fused together so that three alternate carbon atoms in each ring are shared by three rings and bonded to three nearest-neighbor carbon atoms and one hydrogen atom while the remaining seven alternate carbon atoms are shared by two rings and bonded to two carbon and two hydrogen atoms. The former carbon atoms are referred to as tertiary atoms ( $C_t$ ) and the latter as secondary carbon atoms ( $C_s$ ). Electron diffraction studies of gaseous adamantane reveal a mean C-C bond length of  $1.540(2)$  Å with a  $C_t-C_s-C_t$  of  $108.8(10)$  degrees and a  $C_s-C_t-C_s$  of  $109.8(5)$  degrees (ref 7). The low temperature form of adamantane crystallizes in the tetragonal space group  $P4_2/c$  and has a mean C-C of  $1.536$  Å and a  $C_t-C_t-C_t$  of  $108.8$  degrees and a  $C_s-C_t-C_s$  of  $108.9$  degrees (ref 8). This close agreement with the accepted C-C paraffinic single bond length of  $1.541(3)$  Å and the ideal tetrahedral C-C-C bond angle of  $109.47$  degrees indicates the molecular bonding in this caged molecule is not very strained.

In TNA (ref 9) the caged carbon atom configuration is retained with coinciding molecular and crystallographic four-fold inversion axes (4) passing through opposing secondary carbon atoms. Hence, the four symmetry related substituted nitro groups are found on the four tertiary carbon atoms with the mean C-C distance of 1.536 Å (at 300 K); mean  $C_s-C_t-C_s$  of 110.9 and mean  $C_t-C_s-C_t$  of 106.5. Although the C-N distance of 1.529(3) Å is somewhat elongated from the accepted C-N bond of 1.475(10), the mean N-O of 1.210 Å and the O-N-O bond angle of 120 degrees are consistent with accepted values.

The TNA cation consists of the adamantane skeletal carbon cage with four ammonium groups substituted on the four C(1) tertiary carbon atoms (fig. 1). This conformation is quite similar to the atom arrangement found in the previously cited tetra-nitro adamantane. Each ammonium group, which is rotated about 50 degrees from the eclipsed orientation with respect to its hydrogen atoms and the adjacent carbon atoms of the adamantane cage, is defined by the torsion angles: C(2)-C(1)-N(1)-H(1) is 69(3); C(2)-C(1)-N(1)-H(2) is -165(3); C(2)-C(1)-N(1)-H(3) is -53(4); C(3)-C(1)-N(1)-H(1) is -171(3); C(3)-C(1)-N(1)-H(2) is -45(3); and, C(3)-C(1)-N(1)-H(3) is 67(4).

The C-C bond lengths (table 6) are equivalent with C(1)-C(3) of 1.527(4), C(1)-C(3) of 1.531(4) and C(1)-C(2) of 1.533(4) Å, respectively with an average value of 1.530 Å. This agrees with the mean C-C values found in adamantane and TNA. The mean  $C_s-C_t-C_s$  is 110.4 degrees with C(3)-C(1)-C(3), C(3)-C(1)-C(2) and C(3)-C(1)-C(2) having values of 110.3(2) degrees, 110.2(2) degrees, and 110.7(2) degrees, respectively. The mean  $C_t-C_s-C_t$  is 107.5 degrees with C(1)-C(2)-C(1) and C(1)-C(3)-C(1) (table 6) having values of 107.3(3) degrees and 107.7(2) degrees, respectively. These are not significantly different from the C-C-C values found in adamantane and TNA. The C-N distance is 1.499(4) Å which is less elongated than the C-N distance observed in TNA. The C-C-N bond angles are 108.9(2) degrees, 108.8(2) degrees, and 107.9(2) degrees with a mean value of 108.5 degrees.

## CONCLUSIONS

1. The crystal structure positively confirms that the compound synthesized is, indeed, the target compound TAATN.
2. The adamantane heavy atom skeletal cage is a stable molecular configuration which is not perturbed or altered during the reaction scheme used to synthesize TAATN. This suggests that other reactions schemes employed to make other adamantane candidate derivatives may also have little effect upon the adamantane cage conformation.
3. The density of TAATN (1.643 gm/cm<sup>3</sup>) is greater than the density of TEAN.

## **RECOMMENDATIONS**

1. Determine physical properties of TAATN such as thermal sensitivity, impact sensitivity, heat of combustion, and heat of explosion.
2. Initiate a parametric study of a liquid propellant analog of LP1846 which has TAATN substituted for TEAN.
3. Synthesize the tetra-nitro derivative (TATNATN) of TAATN and characterize it with respect to its suitability as an LP fuel candidate.
4. Search for new high energy density fuel candidates.

Table 1. Selected properties of LP1846

Gravimetric Impetus	892 J/g
Volumetric Impetus	1293 J/cm
Flame Temperature	2450 K
Density	1.45 g/cm <sup>3</sup>
Incompatibility	Iron, Copper

Table 2. Atomic coordinates and Beq for TAATN and their esd's

<u>Atom</u>	<u>x</u>	<u>y</u>	<u>z</u>	<u>Beq</u>
TAA cation				
C(1)	0.8883(3)	-0.0513(3)	0.4027(3)	1.0(1)
C(2)	1.0000	0.0	0.3016	1.0(2)
C(3)	0.8345(3)	0.0619(3)	0.4991(3)	1.0(1)
N(1)	0.7783(3)	-0.1021(3)	0.3052(3)	1.2(1)
H(1)	0.807(4)	-0.172(4)	0.264(5)	2.3(9)
H(2)	0.697(5)	-0.113(5)	0.365(6)	5(1)
H(3)	0.757(5)	-0.042(5)	0.243(6)	4(1)
H(4)	0.797(4)	0.141(4)	0.436(4)	1.9(8)
H(5)	0.761(4)	0.031(4)	0.562(4)	1.5(7)
H(6)	0.971(4)	0.073(4)	0.232(4)	1.9(7)
Nitrate anion				
N(2)	0.7017(3)	0.0263(3)	-0.0250(3)	1.2(1)
O(1)	0.7620(3)	0.0959(2)	0.0679(3)	2.0(1)
O(2)	0.6951(2)	0.0602(2)	-0.1595(2)	1.9(1)
O(3)	0.6443(2)	-0.0785(2)	0.0173(3)	1.64(9)

Table 3. Thermal parameters for TAATN and their esd's

<u>Atom</u>	<u>U11</u>	<u>U22</u>	<u>U33</u>	<u>U12</u>	<u>U13</u>	<u>U23</u>
TAA cation						
C(1)	0.009(1)	0.013(1)	0.016(1)	-0.004(1)	-0.002(1)	-0.003(1)
C(2)	0.010(2)	0.011(2)	0.017(1)	-0.001(1)	0.	0.
C(3)	0.006(1)	0.013(1)	0.018(1)	-0.000(1)	0.002(1)	0.001(1)
N(1)	0.010(1)	0.017(2)	0.020(1)	-0.003(1)	-0.004(1)	-0.002(1)
H(1)	0.03(1)					
H(2)	0.06(1)					
H(3)	0.05(1)					
H(4)	0.02(1)					
H(5)	0.019(9)					
H(6)	0.02(1)					
Nitrate anion						
N(2)	0.012(1)	0.016(1)	0.018(1)	0.003(1)	0.004(1)	0.002(1)
O(1)	0.027(1)	0.016(1)	0.032(1)	-0.005(1)	-0.015(1)	-0.004(1)
O(1)	0.027(1)	0.028(1)	0.019(1)	-0.002(1)	0.004(1)	0.003(1)
O(3)	0.023(1)	0.015(1)	0.024(1)	-0.005(1)	0.001(1)	0.003(1)

Table 4. Details of hydrogen bonding with distance in angstroms (A) and angles in degrees

<u>D-----H.....A</u>	<u>D--H</u>	<u>H...A</u>	<u>D.....A</u>	<u>Angle</u>
N(1)-H(1)..O(2)	0.84(4)	2.11(4)	2.914(4)	160(4)
N(1)-H(2)..O(3)	0.99(5)	1.84(6)	2.799(4)	164(4)
N(1)-H(3)..O(1)	0.85(5)	2.10(6)	2.914(4)	163(5)

Table 5. Close heavy atom non-hydrogen bonded interionic distances and their esd's

<u>atom (1)</u>	<u>atom (2)</u>	<u>distance</u>	<u>atom (1)</u>	<u>atom (2)</u>	<u>distance</u>
C(1)	C(1)	2.470(5)	C(3)	C(3)	2.510(4)
C(2)	C(3)	2.521(4)	C(1)	C(3)	2.925(4)
N(1)	O(3)	2.925(4)			

Table 6. Bond lengths and bond angles and their esd's in parentheses

<u>Atom</u>	<u>Atom</u>	<u>distance</u>	<u>Atom</u>	<u>Atom</u>	<u>Atom</u>	<u>Angle</u>
TAA cation						
C(1)	C(2)	1.533(4)	C(1)	C(2)	C(1)	107.3(3)
C(1)	C(3)	1.527(4)	C(1)	C(3)	C(1)	107.7(2)
C(1)	C(3)	1.531(4)	C(3)	C(1)	C(3)	110.3(2)
C(1)	N(1)	1.499(4)	C(3)	C(1)	C(2)	110.2(2)
N(1)	H(1)	0.84(4)	C(3)	C(1)	C(2)	110.7(2)
N(1)	H(2)	0.99(5)	C(1)	N(1)	H(1)	107(3)
N(1)	H(3)	0.85(5)	H(1)	N(1)	H(3)	112(5)
C(2)	H(6)	1.01(4)	H(1)	N(1)	H(2)	115(4)
C(2)	H(6)	1.01(4)	H(3)	N(1)	H(2)	104(4)
C(3)	H(4)	1.04(4)	C(1)	N(1)	H(3)	109(3)
C(3)	H(5)	0.98(4)	C(1)	N(1)	H(2)	109(3)
			N(1)	C(1)	C(3)	108.9(2)
			N(1)	C(1)	C(3)	108.8(2)
			N(1)	C(1)	C(2)	107.9(2)
			H(6)	C(2)	H(6)	103(4)
			H(6)	C(2)	C(1)	114(2)
			H(6)	C(2)	C(1)	110(2)
			H(6)	C(2)	C(1)	110(2)
			H(6)	C(2)	C(1)	114(2)
			H(5)	C(3)	H(4)	107(3)
			H(5)	C(3)	C(1)	111(2)
			H(5)	C(3)	C(1)	110(2)
			H(4)	C(3)	C(1)	113(2)
			H(4)	C(3)	C(1)	109(2)
Nitrate anion						
N(2)	O(1)	1.248(4)	O(1)	N(2)	O(2)	119.4(3)
N(2)	O(2)	1.257(4)	O(1)	N(2)	O(3)	120.9(3)
N(2)	O(3)	1.256(4)	O(2)	N(2)	O(3)	119.7(3)



Table 7. Torsion angles and their esd's for TAA cation

<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>angle</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>angle</u>
N(1)	C(1)	C(3)	H(5)	60(2)	C(2)	C(1)	N(1)	H(2)	-161(4)
N(1)	C(1)	C(3)	H(4)	-59(2)	C(2)	C(1)	C(3)	H(5)	109(4)
N(1)	C(1)	C(3)	H(5)	-97(1)	C(2)	C(1)	C(3)	H(4)	-75(2)
N(1)	C(1)	C(3)	H(4)	-118(1)	C(2)	C(1)	C(3)	H(5)	-79(1)
N(1)	C(1)	C(3)	H(6)	59(2)	C(1)	C(2)	C(1)	H(4)	-63(1)
N(1)	C(1)	C(2)	H(6)	-56(2)	C(3)	C(1)	N(1)	H(1)	-171(3)
C(2)	C(1)	N(2)	H(1)	69(3)	C(3)	C(1)	N(1)	H(3)	67(4)
C(2)	C(1)	N(1)	H(3)	-53(4)	C(3)	C(1)	N(1)	H(2)	-45(3)
C(2)	C(1)	N(1)	H(2)	-165(3)	C(3)	C(1)	C(2)	H(6)	-60(2)
C(2)	C(1)	C(3)	H(5)	178(2)	C(3)	C(1)	C(2)	H(6)	-175(2)
C(2)	C(1)	C(3)	H(4)	59(2)	C(3)	C(1)	N(1)	H(1)	-169(4)
C(2)	C(1)	C(3)	H(5)	145(1)	C(3)	C(1)	N(1)	H(3)	62(4)
C(2)	C(1)	C(3)	H(4)	123(1)	C(3)	C(1)	N(1)	H(2)	-42(3)
C(2)	C(1)	N(1)	H(1)	65(3)	C(3)	C(1)	C(2)	H(6)	75(2)
C(2)	C(1)	N(1)	H(3)	-49(3)	C(3)	C(1)	C(2)	H(6)	-103(5)

Table 8. Nitrate ion best least-squares-plane data and their esd's

<u>Atom</u>	<u>Distance from plane, Å</u>
N(2)	0.004(3)
O(1)	-0.001(2)
O(2)	-0.001(2)
O(3)	-0.001(2)

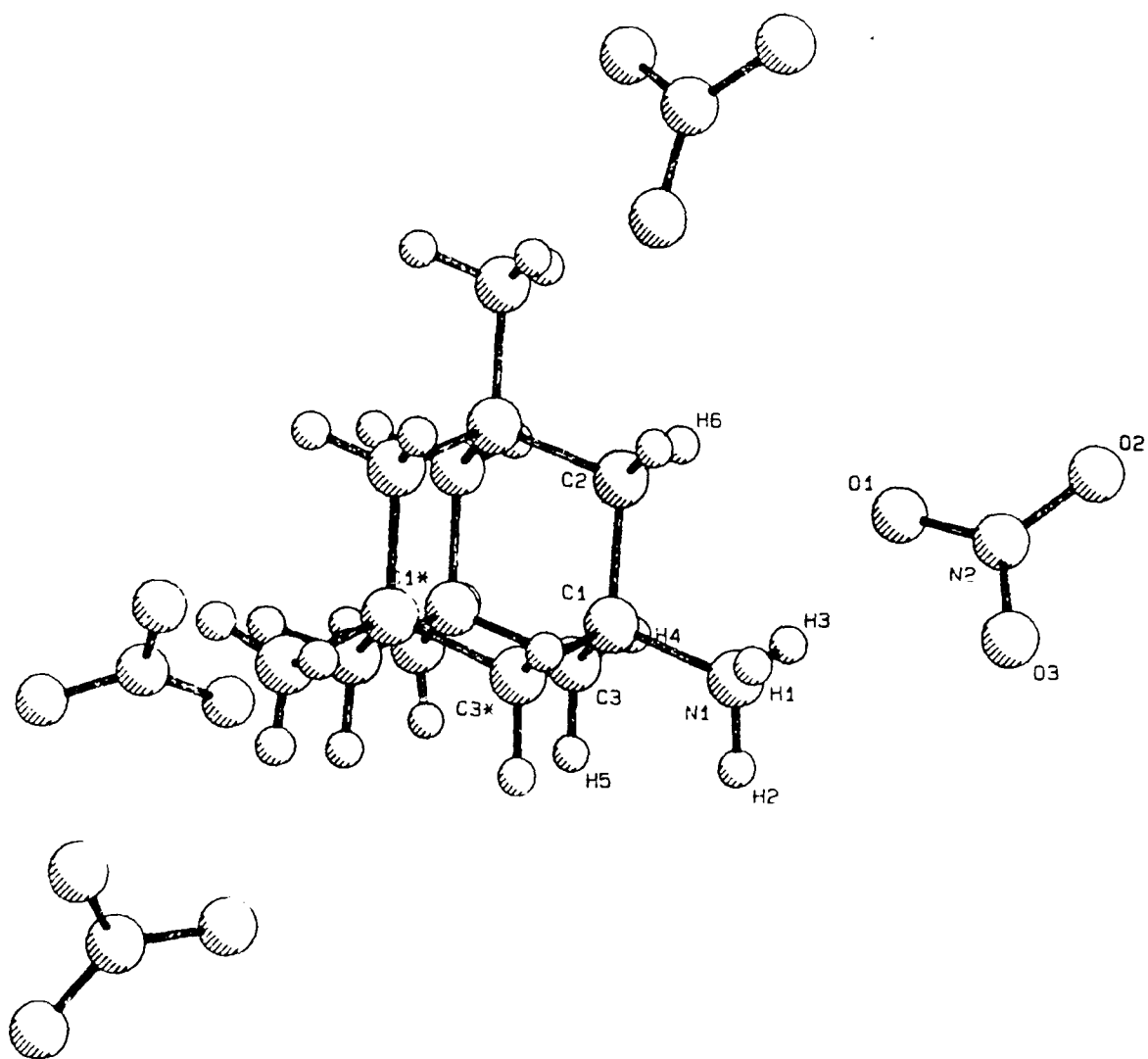


Figure 1. TAATN cation and nitrate anions with atom numbering scheme.

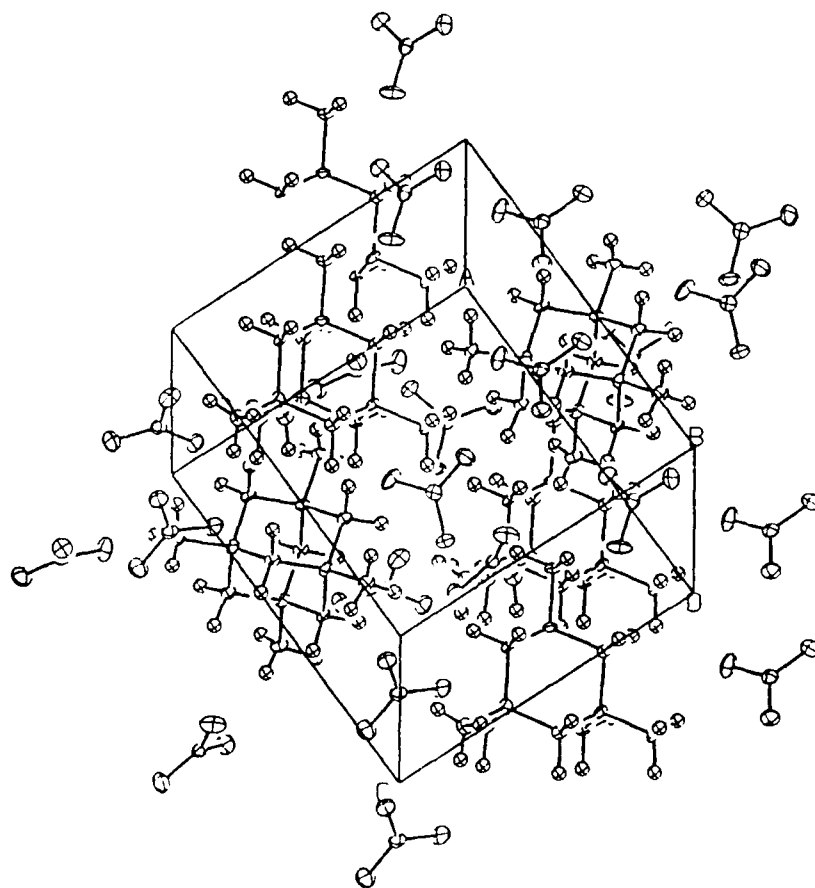


Figure 2. Unit cell of TAATN viewed down the c axis.

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